

# DATA EVALUATION RECORD

## STUDY 3

CHEM 112600	Prohexadione calcium	§161-3
CAS No. 127277-53-6		
FORMULATION--00-ACTIVE INGREDIENT		

STUDY ID 44457784

Venkatesh, K. 1995. Photolysis of <sup>14</sup>C-BAS 125 W on soil. BASF Report No. M9512. BASF Reg. Doc. 95/5187. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC.

DIRECT REVIEW TIME = 43 Hours

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## CONCLUSIONS

### Degradation - Photodegradation on Soil

1. This study is scientifically valid and provides non-upgradable supplemental information that prohexadione calcium is photolytically stable on soil and indicates that prohexadione calcium degrades through microbial-mediated processes.
2. This study is supplemental because of a difference in the half-lives of the irradiated and dark control samples. A prohexadione calcium half-life in the irradiated soil sample was 32.4 days whereas a half-life in the dark control soil sample was 3.1 days. The much longer half-life of the irradiated sample compared to the dark control appeared to be soil viability related and/or moisture content related (see the Reviewers' Comments 2)

The study results were as follows:

A. Cyclohexene ring-labeled [3,5-<sup>14</sup>C]prohexadione calcium at a nominal application rate of 2.8 ppm degraded with a EFED-calculated linear half-life of 16.2 days ( $r^2 = 0.82$ ) in the continuously irradiated (with a xenon arc lamp) loamy sand soil maintained at  $25 \pm 1^\circ\text{C}$ . The degradation half-life was 32.4 days when corrected for the day:night irradiation period, 12 hours irradiation:12 hours of darkness. The major degradate was despropionyl. It was present at a maximum of about 15% at days 7 and 15 posttreatment. Evolved <sup>14</sup>CO<sub>2</sub> accounted for a maximum of 20.4% of the applied at 10 days posttreatment. Other volatiles accounted for no more than 0.2% at any time.

B. In the dark control cyclohexene ring-labeled [3,5-<sup>14</sup>C]prohexadione calcium degraded with a linear half-life of 3.1 days. Dispropionyl was a maximum of 6.0% of the applied radioactivity on the 3rd day posttreatment. Evolved <sup>14</sup>CO<sub>2</sub> was a maximum of 77.8% at 15 days posttreatment; [<sup>14</sup>C]organic volatiles were negligible.

The dark control half-life (a linear first order kinetics  $T_{1/2} = 3.1$  days) is in fairly close agreement with the aerobic soil metabolism half-life (a linear first order kinetics  $T_{1/2} = 9.8$  days,  $r^2 = 0.73$ ; a nonlinear first order kinetics  $T_{1/2} = 1.4$  days,  $r^2 = 0.98$ ; MRID 44457785) pointing to the microbial-mediated processes as the important route of prohexadione calcium degradation.

3. Regardless of the study shortcomings no additional information is required on photolysis of prohexadione calcium in soil at the present time. Repeating the study will not provide any more information than has already been concluded based on this study results.

## METHODOLOGY

Samples (10 g) of sieved (2 mm) loamy sand soil (collected from Holly Springs, NC; 77% sand, 16% silt, 7% clay, 1.9% organic matter, pH 6.1, CEC 6.5 meq/100 g; Table 2, p. 27) were weighed into individual sterile Petri dishes and treated by syringe with cyclohexene ring-labeled [3,5-<sup>14</sup>C]prohexadione calcium (calcium 3-oxido-4-propionyl-5-oxo-3-cyclohexenecarboxylate; radiochemical purity varied from 94.9 to 97.02%, specific activity 15.3 mCi/mmol; p. 10), dissolved in acetonitrile and 1 N HCL (unspecified volume ratio), at a nominal rate of 2.8 ppm (2.75-2.79 ppm). The samples were placed in an incubation chamber equipped with two cooling jackets (top and bottom) to maintain the temperature at  $25 \pm 1^\circ\text{C}$ , and covered with a quartz plate (p. 11; Figure 5, p. 41). Moist, CO<sub>2</sub>-free, filtered (0.2  $\mu\text{m}$ ) air was drawn through the chamber then passed through an ethylene glycol trap, 0.1 N sulfuric acid, and two sodium hydroxide traps in succession (p. 12). Samples were irradiated continuously for up to 360 hours (15 days) using a xenon arc lamp equipped with a filter to absorb UV radiation of  $\leq 290\text{ nm}$ ; soil moisture was adjusted to 75% of the soil moisture content at 0.33 bar through the periodic addition of water (see Comment #2) and temperature was monitored daily using a probe placed on the soil surface. The intensity of the light source was measured with a light intensity meter throughout the study; the intensity of the source was determined to be 1900  $\mu\text{E}/\text{m}^2/\text{sec}$  which was equivalent to that recorded for natural sunlight on a clear day in North Carolina, during mid-November (p. 11). A graph of the artificial and natural light sources was presented in Figure 4 (p. 40). Dark control samples of loamy sand soil were prepared as described previously except Erlenmeyer flasks were used. The samples were treated with 2.45-2.77 ppm of cyclohexene ring-labeled [3,5-<sup>14</sup>C]prohexadione calcium and incubated in darkness at  $25 \pm 1^\circ\text{C}$  for up to 360 hours (15 days; p. 13). Samples of irradiated and dark control soils were removed for analysis at 0, 3, 7, 10, and 15 days posttreatment (p. 14). Volatile traps were removed for analysis and replaced regularly throughout the incubation period.

Soil samples were extracted three times using acetonitrile:1 N sulfuric acid (12:4, v:v; two times, first extraction) and acetonitrile (two times, second extraction), followed by a Soxhlet extraction with acetonitrile for 6-8 hours (third extraction, p. 15; Figure 6, p. 42). Following each extraction, aliquots of the extracts were analyzed for total radioactivity by LSC. The second and third soil extracts were not analyzed further because they contained low percentages of radioactivity - no more than 8.2% of the applied (Table 6, see THE REVIEWERS' COMMENT 7). The acetonitrile:1 N sulfuric acid extracts were analyzed via HPLC (Hamilton PRP-1 column) using a mobile phase gradient of 0.01% acetic acid in water:acetonitrile (95:5 to 10:90 to 5:95, v:v) and HPLC (YMC-OD AQ column) using a mobile phase gradient of 0.1% trifluoroacetic acid in acetonitrile:0.1% trifluoroacetic acid in water (5:95 to 100:0, v:v) with radioactive flow detection; eluate fractions were collected in one-minute intervals and analyzed for total radioactivity by LSC (p. 15). Both HPLC systems yielded similar results (pp. 16-17). Samples were co-chromatographed with nonradiolabeled reference standards. Next the soil was air dried, weighed, combusted, and remaining radioactivity was determined.

To determine nonextractable bound [ $^{14}\text{C}$ ]residues, selected samples (15 days posttreatment) were further extracted by refluxing with sodium hydroxide for 2 hours (p. 15; Figure 7, p. 43). Following centrifugation, the supernatant was decanted, partitioned three times with dichloromethane, and centrifuged. The resulting organic phase layer was analyzed for total radioactivity by LSC. The aqueous layer was acidified (pH 1, HCl) to precipitate humic acids and centrifuged, and the supernatant was decanted. The supernatant was analyzed by LSC, extracted with ethyl acetate, and partitioned into two layers. The organic layer (fulvic acid fraction) and the aqueous layer were analyzed for total radioactivity by LSC. The remaining precipitate was redissolved in sodium hydroxide and analyzed for total radioactivity associated with the humic acid fraction by LSC. Post-extracted soil samples were dried, weighed, and analyzed for total radioactivity associated with the humin fraction by LSC following combustion.

Duplicate aliquots of the trapping solutions were analyzed for total radioactivity by LSC. To quantify  $^{14}\text{CO}_2$  in the sodium hydroxide trap solutions, aliquots were acidified ( $5\text{ N H}_2\text{SO}_4$ ) and the released  $^{14}\text{CO}_2$  was captured in scintillation liquid and analyzed by LSC (p. 14). The presence of  $^{14}\text{CO}_2$  was confirmed in the sodium hydroxide trap solution by precipitation with  $\text{BaCl}_2$ .

#### STUDY AUTHOR'S DATA SUMMARY

In the irradiated soil, material balances (based on LSC analysis) were 100.7%-107.2% of the applied radioactivity from 0 to 7 days posttreatment and decreased to 94.6% by 15 days (Table 7, p.32). In the dark control soil, material balances were 86.0%-103.7% of the applied throughout the incubation period with no clear pattern of decline.

Cyclohexene ring-labeled [3,5- $^{14}\text{C}$ ]prohexadione calcium, at a nominal application rate of 2.8 ppm, degraded with a registrant-calculated half-life (reported as a  $\text{DT}_{50}$ ) of 13.6 days ( $r^2 = 0.84$ ) in loamy sand soil maintained at  $25 \pm 1^\circ\text{C}$  and irradiated continuously for up to 15 days with a xenon arc lamp (p. 21; Table 10, p. 35; Figure 19, p. 55). The degradation half-life was determined using the Gustafson model, a first-order nonlinear kinetic model (Gustafson and Holden, 1990). In the dark control soil, prohexadione calcium degraded with a registrant-calculated half-life (reported as a  $\text{DT}_{50}$ ) of 2.5 days ( $r^2 = 0.98$ ) in loamy sand soil maintained at 75% of the soil moisture content at 0.33 bar and  $25 \pm 1^\circ\text{C}$  for up to 15 days (Figure 20, p. 56). In the irradiated soil, the parent compound was initially present at 92.6% of the applied radioactivity, decreased to 73.5% of the applied by 7 days posttreatment, and was 45.1-47.9% at 10-15 days posttreatment (Table 8, p. 33). In the dark control soil, the parent compound was initially present at 92.6% of the applied radioactivity, decreased to 47.1% of the applied by 3 days posttreatment, and was 2.3% at 15 days posttreatment. In the irradiated soil, the major degradate 3-hydroxy-5-oxo-cyclohexene-1-carboxylic acid (BAS 5376) was initially present (day 0) at 3.2% of the applied radioactivity, and increased to 12.6-15.2% of the applied by 7-15 days posttreatment. In the irradiated soils, nonextractable [ $^{14}\text{C}$ ]residues were initially (day 0) 0.25% of the applied radioactivity and increased to 10.3% by 10-15 days posttreatment (Table 7, p. 32);

[ $^{14}\text{C}$ ]residues associated with the humic acid, fulvic acid, and humin fractions were 1.6%, 3.1%, and 1.0% of the applied, respectively, at 15 days posttreatment (Table 11, p. 36). Uncharacterized [ $^{14}\text{C}$ ]residues were initially (day 0) 1.5% of the applied radioactivity and increased to 9.0% by 15 days posttreatment. For the irradiated samples, evolved  $^{14}\text{CO}_2$  was 1.6% of the applied radioactivity at 3 days posttreatment and accounted for 11.9-20.4% of the applied at 10-15 days posttreatment; [ $^{14}\text{C}$ ]organic volatiles were  $\leq 0.20\%$  of the applied. In the dark control soil, the minor degradate BAS 5376 was present at 3.2-6.0% of the applied radioactivity from 0 to 15 days posttreatment. Nonextractable [ $^{14}\text{C}$ ]residues were initially (day 0) 0.25% of the applied radioactivity, increased to a maximum of 22.0% by 10 days posttreatment and were 16.9% at 15 days posttreatment; [ $^{14}\text{C}$ ]residues associated with the humic acid, fulvic acid, and humin fractions were 5.5%, 1.6%, and 2.4% of the applied, respectively, at 15 days posttreatment. Uncharacterized [ $^{14}\text{C}$ ]residues were  $\leq 1.7\%$  of the applied radioactivity. Evolved  $^{14}\text{CO}_2$  was 26.5% of the applied radioactivity at 3 days posttreatment, increased to 61.6% of the applied by 7 days posttreatment, and accounted for 77.8% at 15 days posttreatment; [ $^{14}\text{C}$ ]organic volatiles were negligible.

#### THE REVIEWERS' COMMENTS

1. This study shows that prohexadione calcium is stable to photodegradation on soil and instead microbial mediated processes are major degradation pathway. This study is supplemental, non-upgradable, because the half-life of the irradiated sample was greater than the half-life of the dark control.
2. In the dark control prohexadione calcium degraded with the linear half-life of 3.1 days. The half-life is in a fairly close agreement with the aerobic soil metabolism half-life which is 9.8 days expressed as a linear first order kinetics  $T_{1/2}$  ( $r^2 = 0.73$ ) or 1.4 days expressed as a nonlinear first order kinetics  $T_{1/2}$  ( $r^2 = 0.98$ ; MRID 44457785). In the continuously irradiated (with a xenon arc lamp) loamy sand soil maintained at  $25 \pm 1^\circ\text{C}$ , prohexadione calcium, at a nominal application rate of 2.8 ppm, degraded with an EFED-calculated linear half-life of 16.2 days ( $r^2 = 0.82$ ). The degradation half-life was 32.4 days when corrected for the day:night irradiation period (12 hours irradiation:12 hours of darkness).

The much longer half-life of the irradiated sample compared to the dark control appeared to be soil viability related or/and moisture content related. The twice daily adjustments of soil moisture to 75% of 0.33 bar by addition of water equivalent to the weight lost by the soil may have been not sufficiently frequent to maintain the moisture content. Additionally, in samples irradiated for more than 7 days moisture content was not adjusted during weekends. Excessive drying of the irradiated soil samples may have resulted in a reduction in microbial populations and/or microbial activity, and have been

the cause of the observed faster prohexadione calcium degradation in the dark controls compared to the irradiated samples.

3. Because the irradiated samples were treated and placed in incubation on five separate days (February 7, 15 and 28, March 7 and May 15), and dark control samples were treated on three separate days (February 28, March 7 and May 15; Table 3, p. 28), the uncertainty in calculated half life is greater than if the irradiated samples were treated at the same time and incubated simultaneously. In addition, single test samples were treated as opposed to recommended duplicate samples. In future studies, the experimental procedures for treatments should be handled in a similar manner for reliable comparisons.
4. The study author stated that a sandy loam soil was used for the dark control samples (p. 13). It could not be determined whether this was a typographical error or a soil (sandy loam) with a different texture than that of the irradiated soil samples (loamy sand) was used. The reviewer referred to the dark control soil as loamy sand throughout the DER. Clarification by the registrant is necessary.
5. Method detection limits for HPLC and LSC were not reported. The study author stated that the second and third soil extracts were not analyzed via HPLC because they contained low percentages of the applied radioactivity (< 8.2%, Figure 6). The authors did not state if the amounts were below the HPLC detection level. EFED believes that the additional extracts analyses via HPLC could altered the calculated half-life.
6. Although this study has a few inefficiencies, repeating the study will not provide any more information than has already been concluded based on this study results. Therefore the study has been classified as non-upgradable supplemental for the fulfillment of the data requirement for the prohexadione calcium (BAS 125 W) soil photolysis study.

## REFERENCES

Gustafson, D.I. and L.R. and Holden, 1990. Nonlinear pesticide dissipation in soil: A new model based on Spatial Variability. *Environ. Sci. and Tech.* 24, pp 1032-1038.

# ProHexadione Calcium

DER MRLD 444577-84

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Pages 7 through 32 are not included.

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